

Lubrication at the Nanoscale

The DOE Center of Excellence for the
Synthesis and Processing of Advanced Materials

Center Review

DOE, Germantown, MD. Thursday June 12, 2003

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ARGONNE NATIONAL
LABORATORY



University of Illinois
Frederick Seitz Materials
Research Laboratory

Los Alamos
NATIONAL LABORATORY

Pacific Northwest National Laboratory



THE TRIBOLOGY PROBLEM



Energy and technology relevance: lubrication; transportation; defense programs; MEMS; biosensors; microfluidics; chemical reactivity at and near surfaces; flow processing of ceramics and polymers; formation and adhesive characteristics of coatings; fundamentals of solid-fluid interface science; the science and technology of interacting surfaces in relative motion.

Main tasks of the group

TASK 1. Synthesis & processing of new surface coatings

FS-MRL, ANL, LANL, SNL/NM

TASK 2. New theoretical and computational advances

SNL/NM, PNNL, ORNL

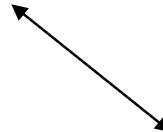
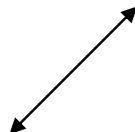
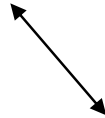
Unifying systems

TASK 3. New spectroscopic and nanoprobe methods

FS-MRL, LANL, SNL/NM, LBNL, UCSD

TASK 4. New insights into relations between nanoscale, microscale, and macroscopic tribology

FS-MRL, ORNL, ANL, UCSD



***Experimental and Computational Lubrication at the Nanoscale
Report of the First Annual Meeting
Held at SNL/NM on March 14, 2003***

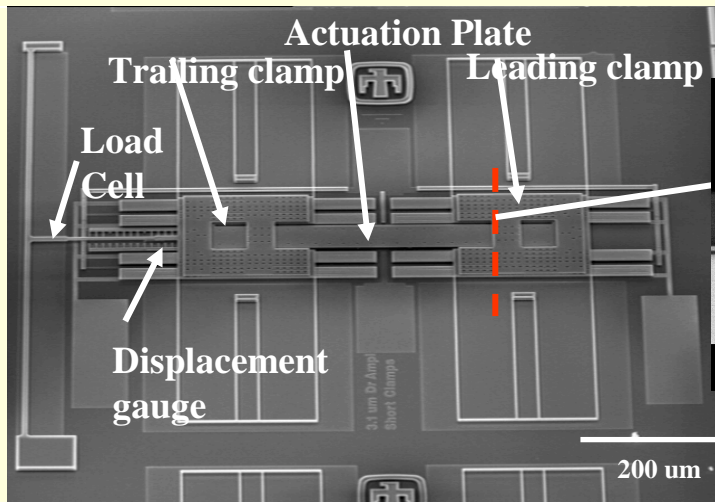
This first meeting of the entire group since the S & P Center was awarded also attracted extensive outside participation. In attendance were:

ANL:	Ali Erdemir, Orlando Auciello
LANL:	Jeanne Robinson
PNNL:	James Cowin
SNL/NM:	Gary Grest, Jack Houston, Marten de Boer, Mike Kent, Mike Chandross, Mark Stevens, Tom Friedmann, Mike Dugger, George Samara
ORNL:	Yehuda Braiman, Peter Cummings
LBNL:	Miquel Salmeron
UCSD:	Sunhil Sinha
UI/FS-MRL:	Steve Granick

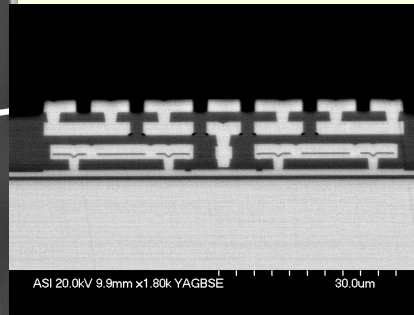
Proposed Areas of Focus:

1. **Confined water and lubrication: SAM coatings, water penetration, chemical degradation**
2. **Confined non-polar fluids and lubrication**
3. **Patterned surfaces, controlled chemical and topographical heterogeneity**

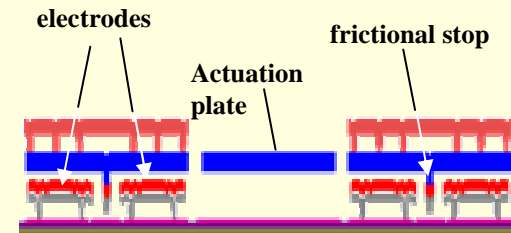
MEMS: Inchworm device



SEM of Friction Clamp

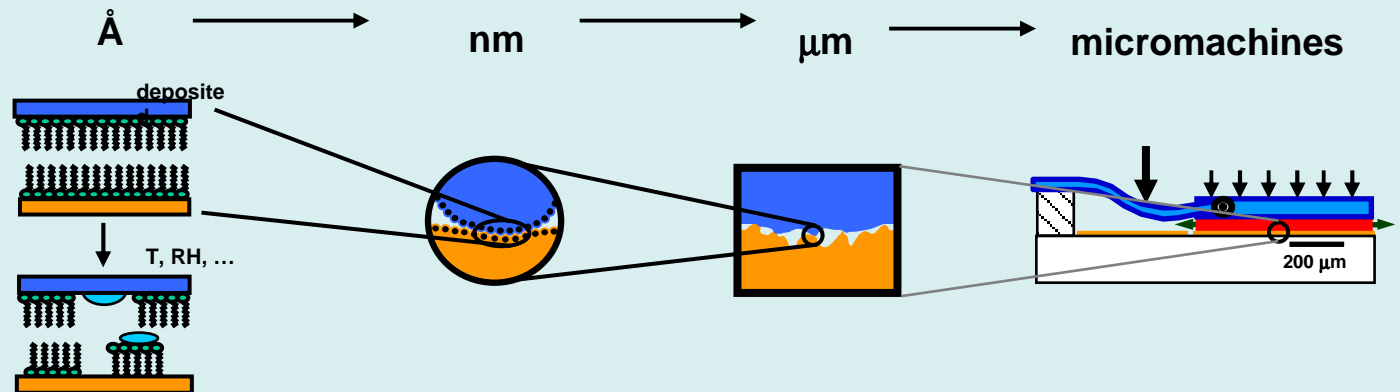


Cross-section(schematic)



Uniformly apply pressure in frictional clamps
can test friction over wide pressure space

Linking the length scales to understand and model adhesion and friction:



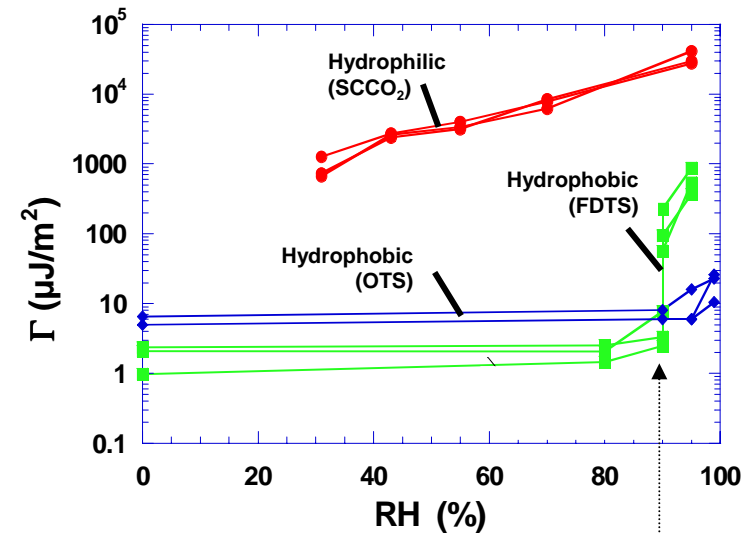
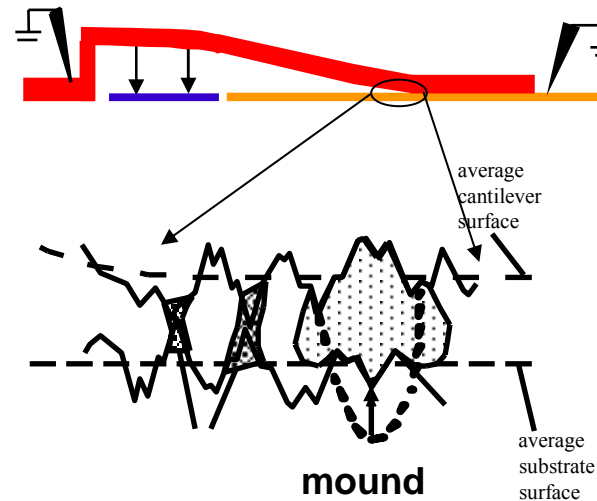
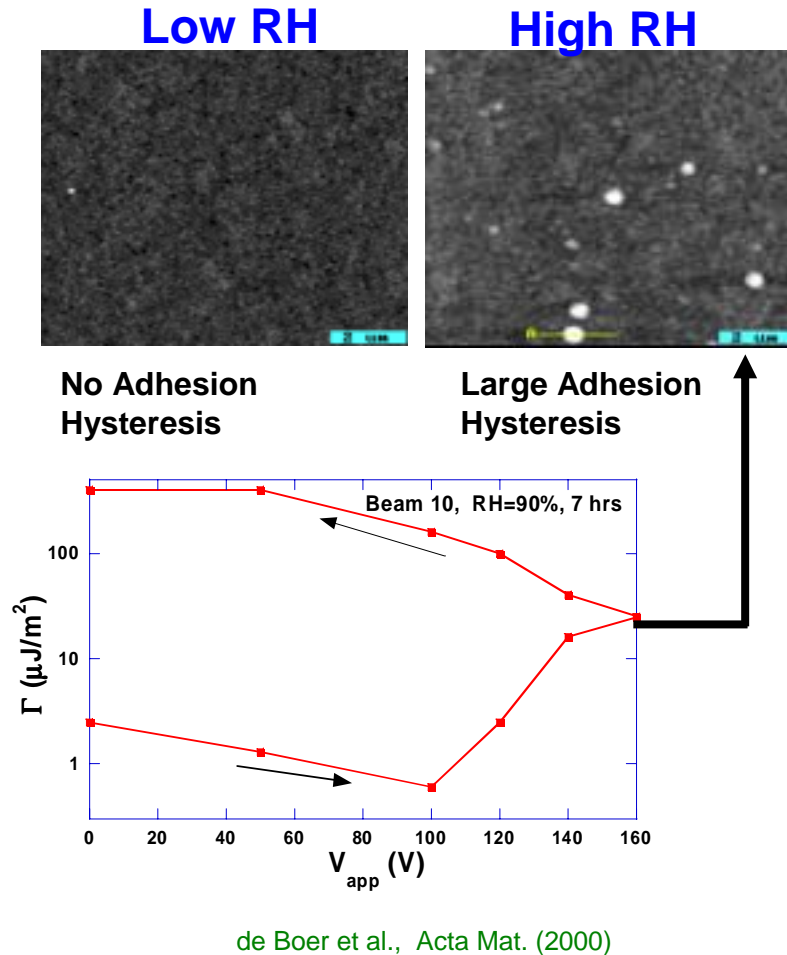
- SAM coatings
- molecular structure
- stability and durability
- environmental degradation

- single asperity
- adhesion energy
- friction coefficient
- dynamics
- atomistic simulation

- multi-asperity
- surface morphology
- 'real' contact simulation

- design rules
- device models
- device performance
- reliability testing

Hydrophobic case (FDTs film): reconfiguration of surface at high RH



What is the mechanism of film degradation ?
Does water penetrate through silane molecules ?

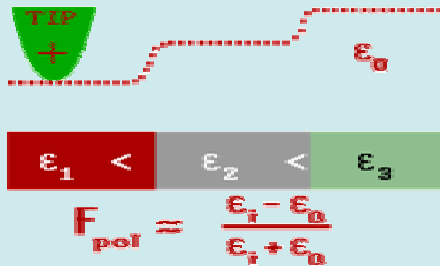
New imaging tools for studies of liquid films and wetting phenomena at the nanometer scale

Combination of AFM techniques

Electrostatic mode:

Scanning Polarization Force Microscopy

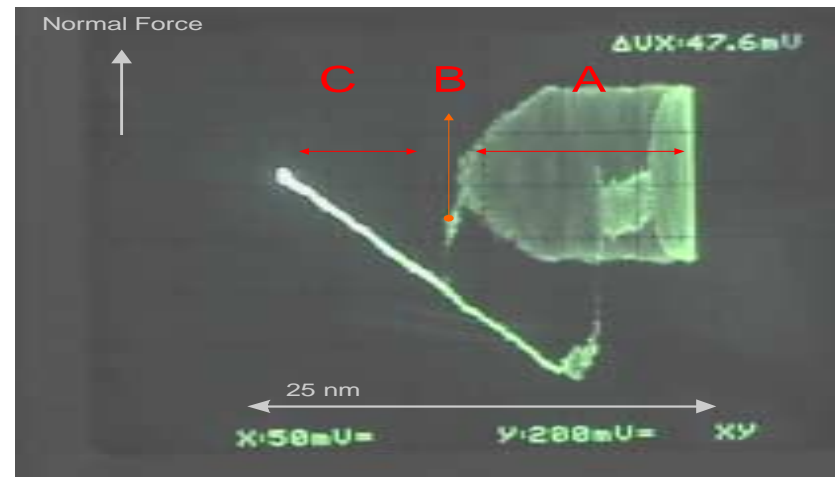
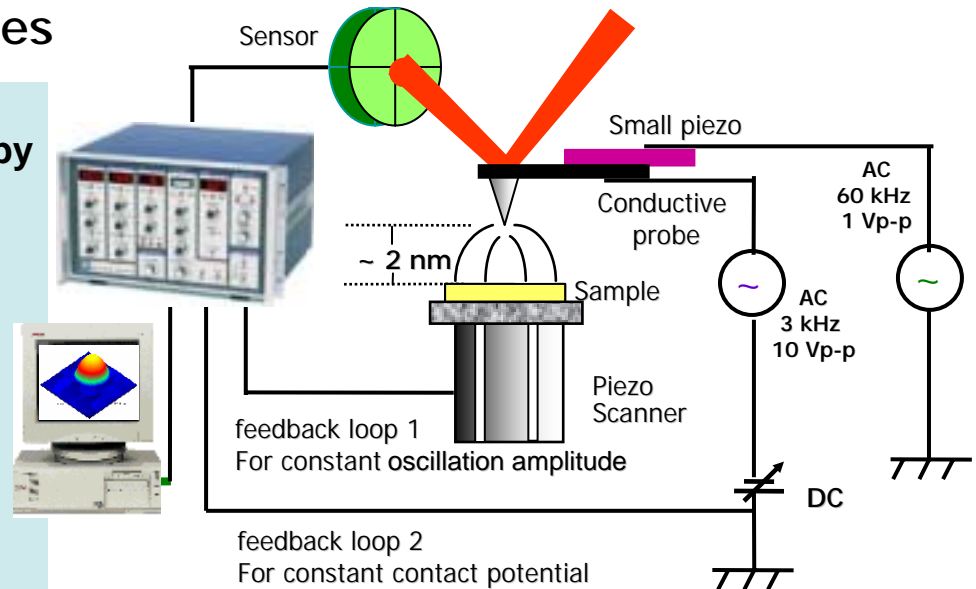
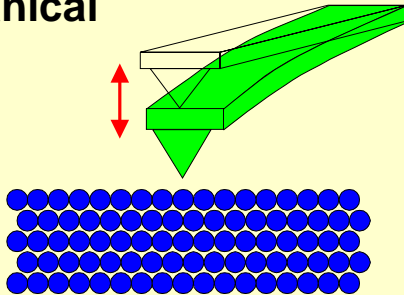
Contrast:



Dielectric Spectroscopy:

Freq. Dependence of $\epsilon(\omega)$

Mechanical



Modulation techniques in SPFM

Electrostatic force for a dielectric material

$$F = \varepsilon_0 \times \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \times f(z) \times (V - \phi)^2$$

Modulating $V = V_0 + V_1 \sin \omega t$

$$F_{dc} = \tilde{\varepsilon}(\omega) \times f(z) \times (V_0 - \phi)^2$$

Topography + surface potential

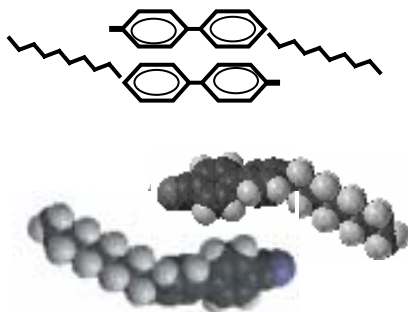
$$F_{\omega} = \tilde{\varepsilon}(\omega) \times f(z) \times (V_0 - \phi) \times V_1$$

Surface potential = Kelvin Probe Microscopy

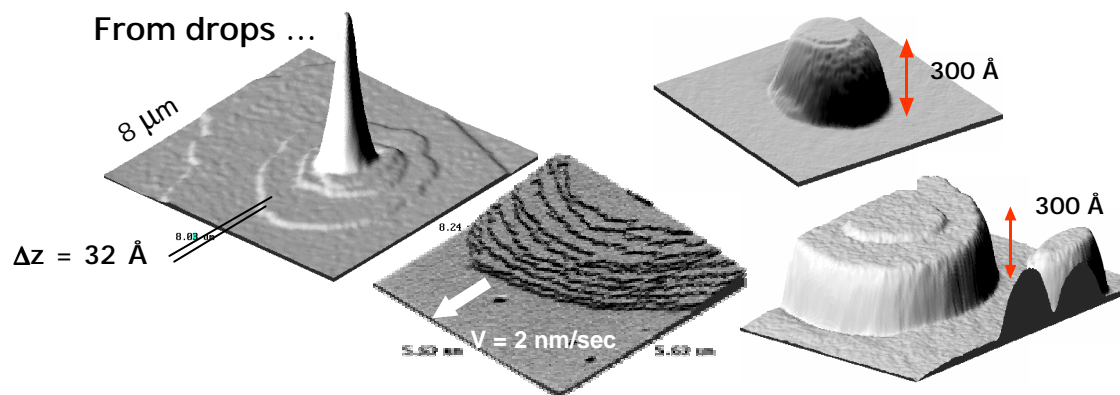
$$F_{2\omega} = \tilde{\varepsilon}(\omega) \times f(z) \times V_1^2 \longrightarrow \text{Topography}$$

Example: Spreading of 8CB liquid crystal on Si

Pairing of 8CB molecules into dimers

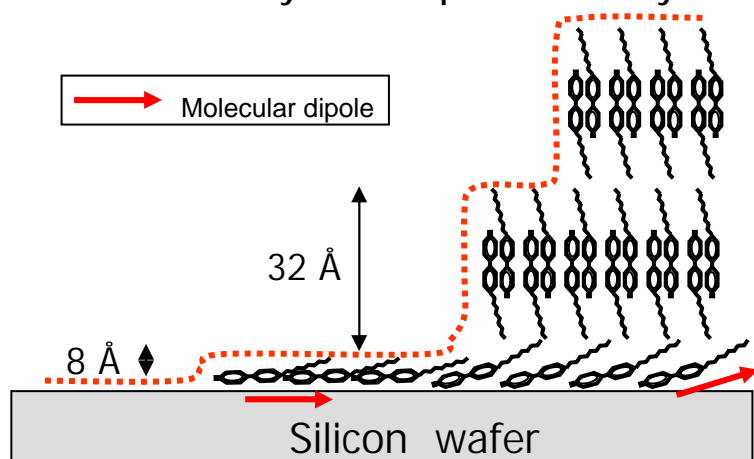


From drops ...



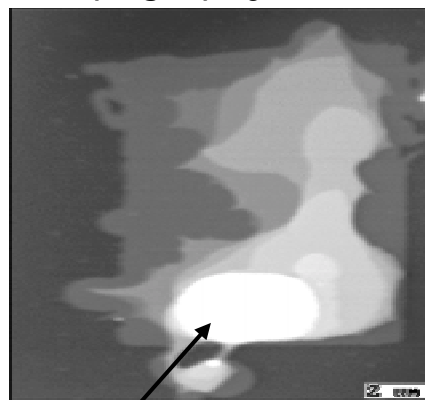
... to final stage of smectic pancakes

Smectic bilayers on top of a monolayer

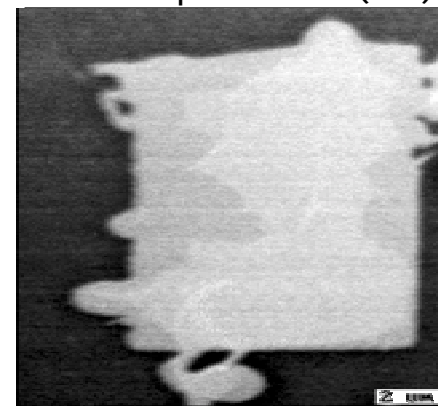


Phys. Rev. Lett. **84**, 1519 (2000)

Topography (2ω)



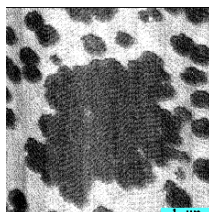
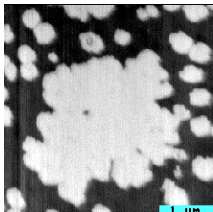
Contact potential (1ω)



Initial isotropic droplet

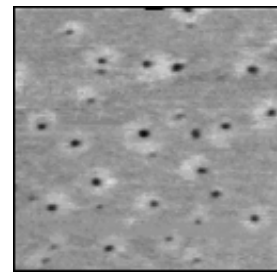
Silanes on mica: Humidity dependence studies

Topo Friction



Hexadecylsilane islands

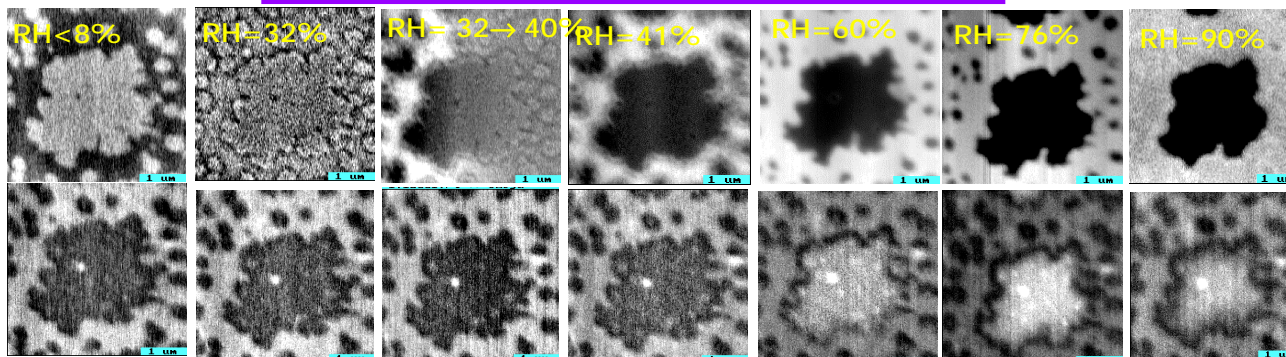
Contact



Octadecylsilane monolayer with pinholes

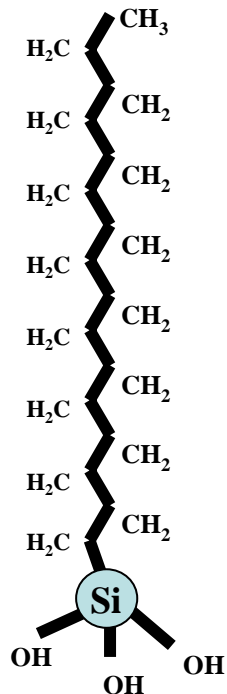
Contact

SPFM (tip ~30 nm over surface)

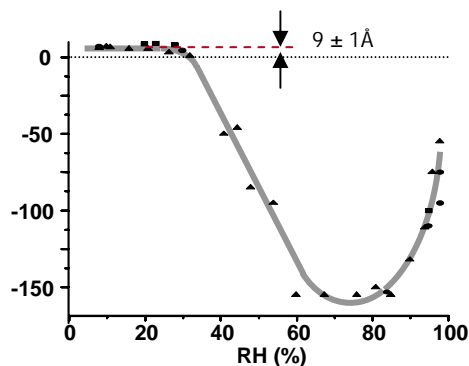


Topography

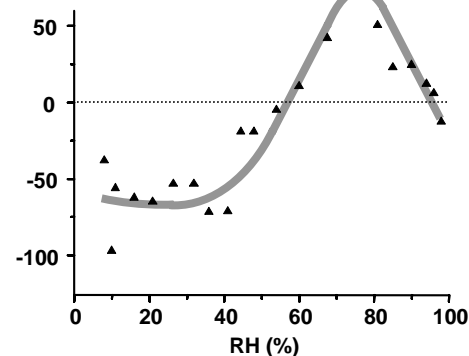
Contact potential



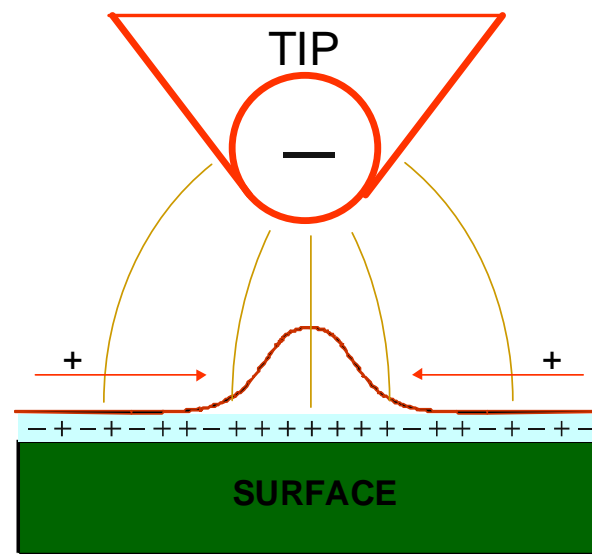
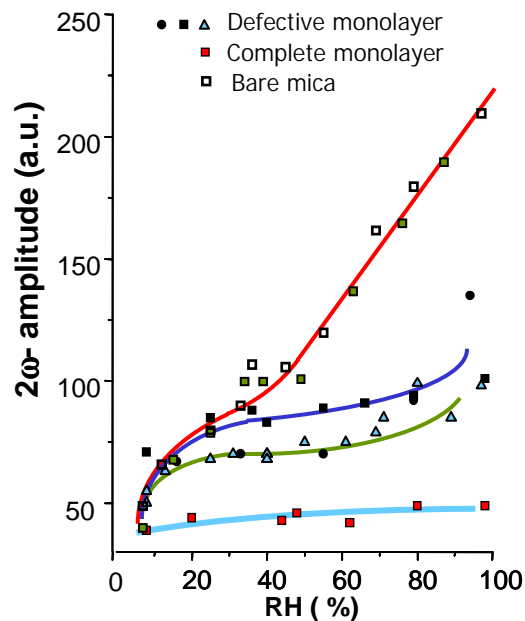
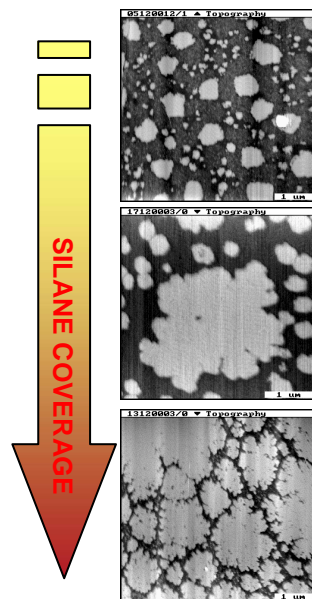
Apparent island height



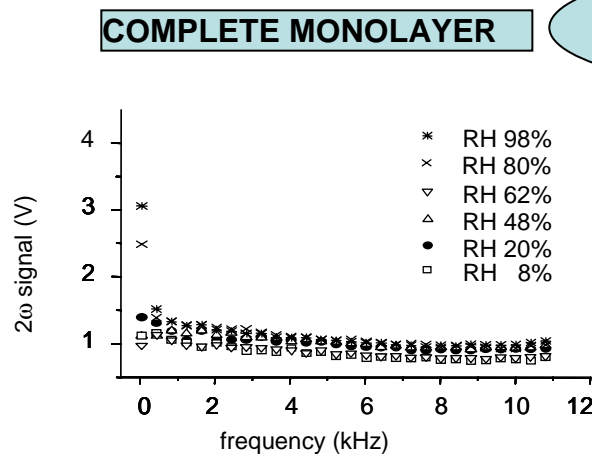
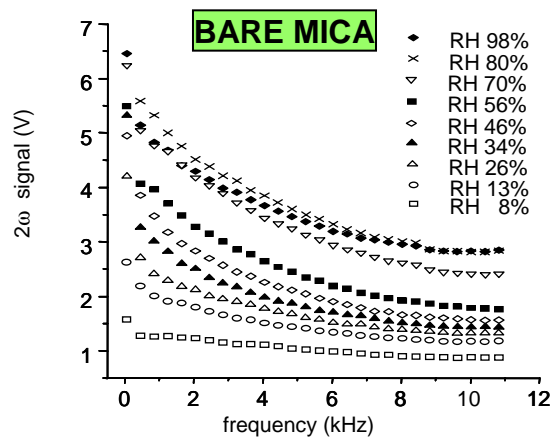
Contact potential contrast



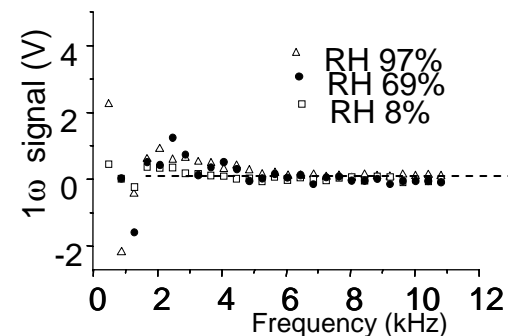
Electrostatic force vs. humidity



Frequency dependence

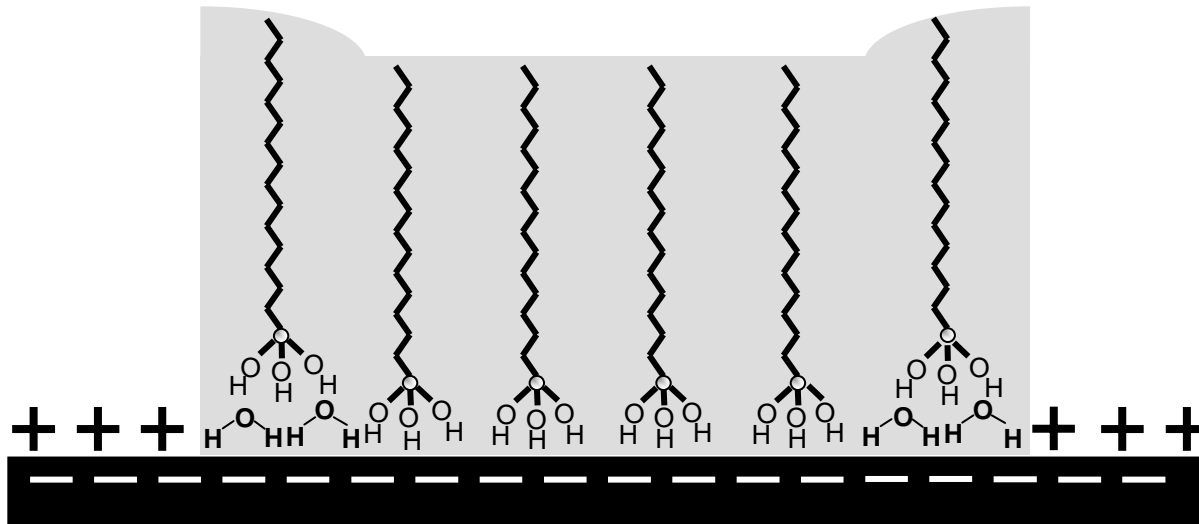


No change in force or contact potential can be observed



Summary:

1. On compact films water cannot penetrate through molecules up to 99% RH
2. On defective films and near island edges (where packing is less-compact) water does penetrate



WATER UPTAKE BY OTS MONOLAYERS

Controlled humidity experiments:

(a) monolayer preparations at systematically varied ambient humidities

(b) exposure of pre-formed OTS monolayers to systematically varied humid ambients

■ In-situ Fourier-transform infrared spectroscopy measurements

- effects on siloxane backbone
- effects on alkyl chain structure
- dependence on monolayer packing density
- water structure at the air and substrate interfaces

■ In-situ atomic force microscopy measurements

- effects on film morphology at nanoscale

■ In-situ imaging ellipsometry and neutron reflectivity studies

(LANSCE, Majewski)

- effects on film thickness

■ In-situ infrared and second harmonic imaging studies (Robinson, LANL)

- monolayer patterns, defects, and water structure

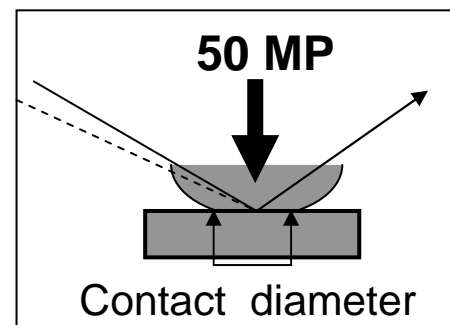
Contact angle measurements (Johal, New College)

A crucial step to advance the science and technology of lubrication is the development of imaging and spectroscopic tools that can interrogate buried interfaces. This area has not yet received the attention it deserves.

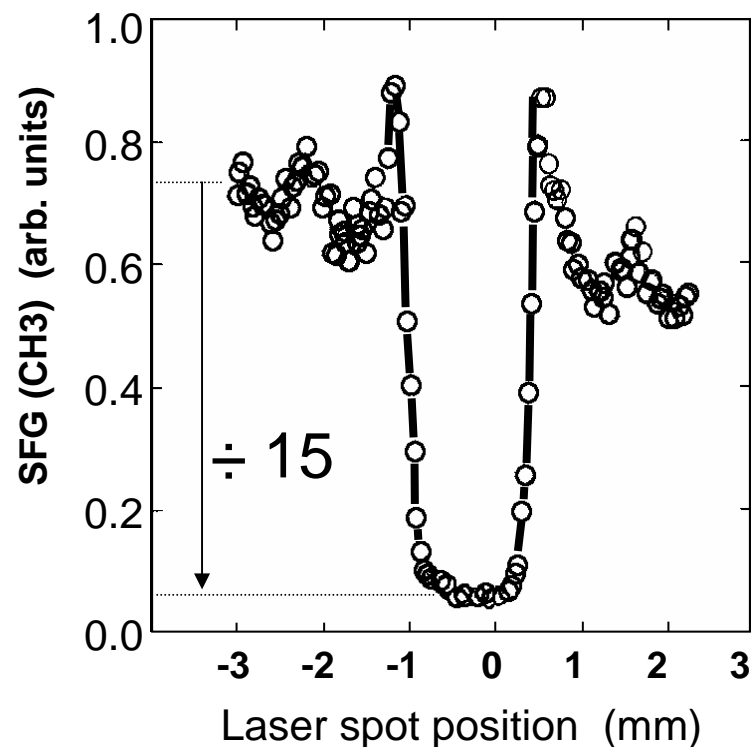
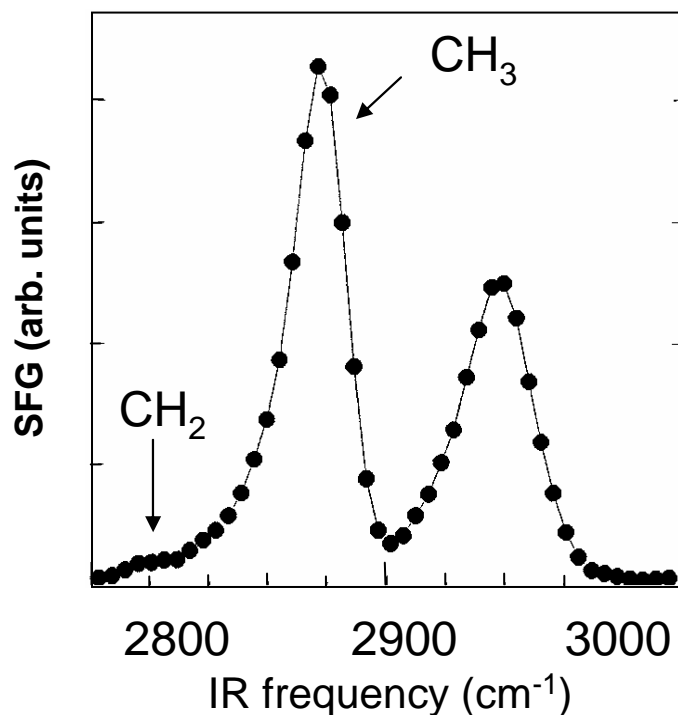
The time is ripe now, with many new advanced technologies, for a big push forward

New Imaging and Spectroscopic Methods: vibrational structure

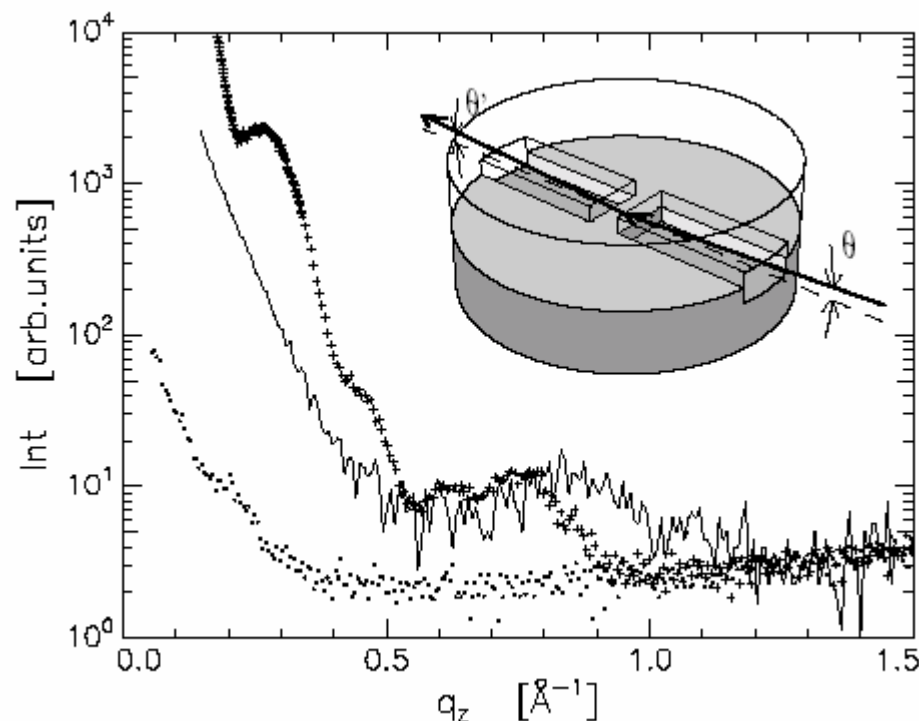
Sum Frequency Generation:



First results: OTS squeezed between a quartz lens and a flat



New Imaging and Spectroscopic Methods: layering structure

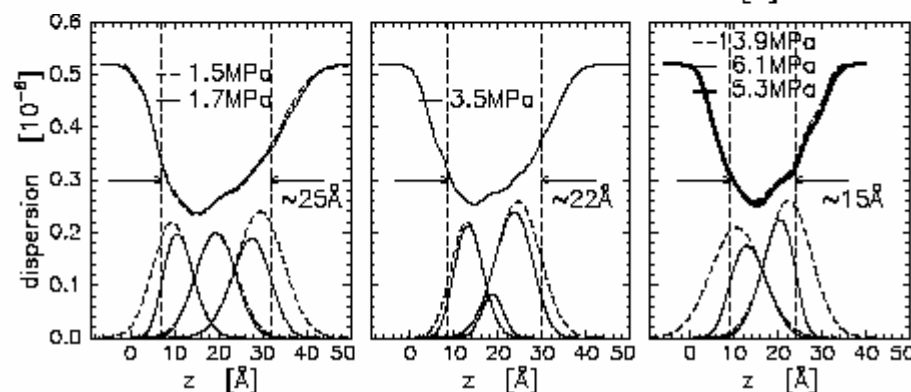
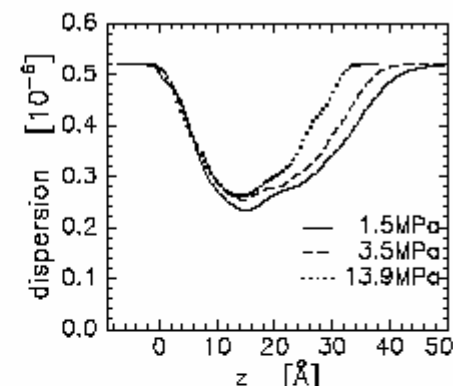


Europhysics Lett.,
2002.

X-ray waveguide approach.

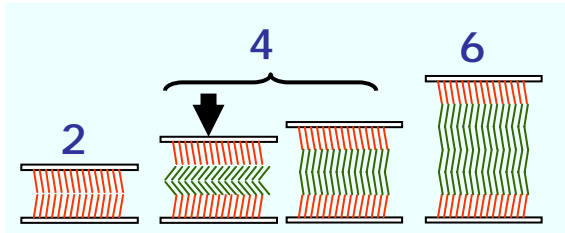
The first direct measurements of molecular layering in confined fluids. Performed at APS.

NEEDED: same for in-plane order; quantitative comparison to simulations with potential of these molecules; do the same during sliding.

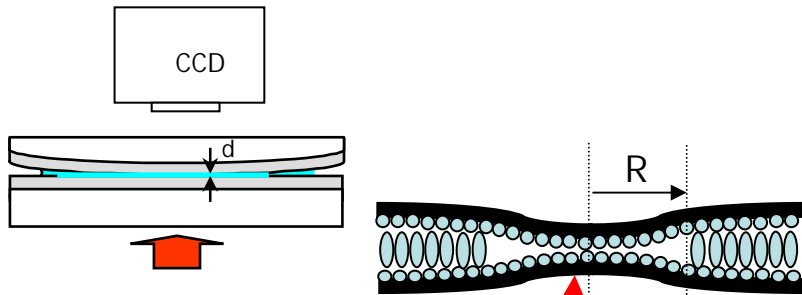


New Imaging and Spectroscopic Methods: diffusion and layering

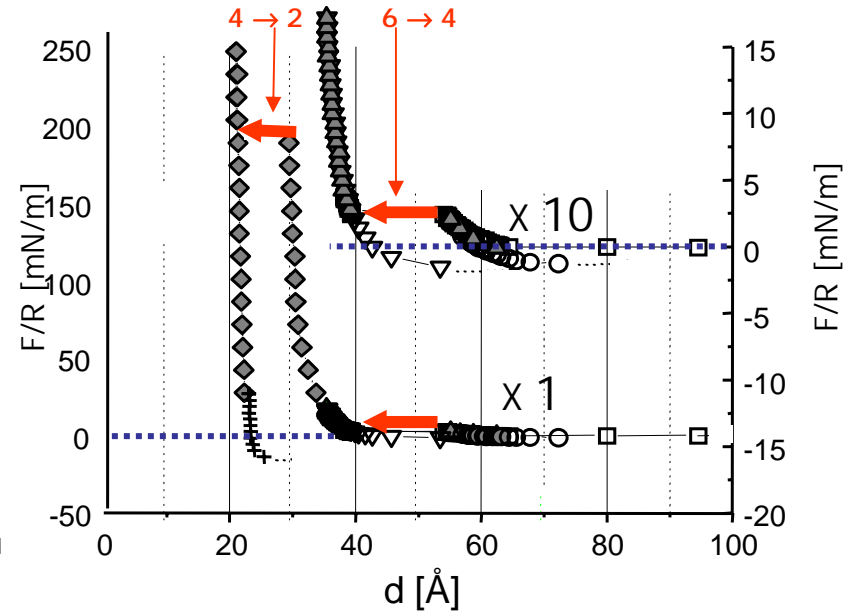
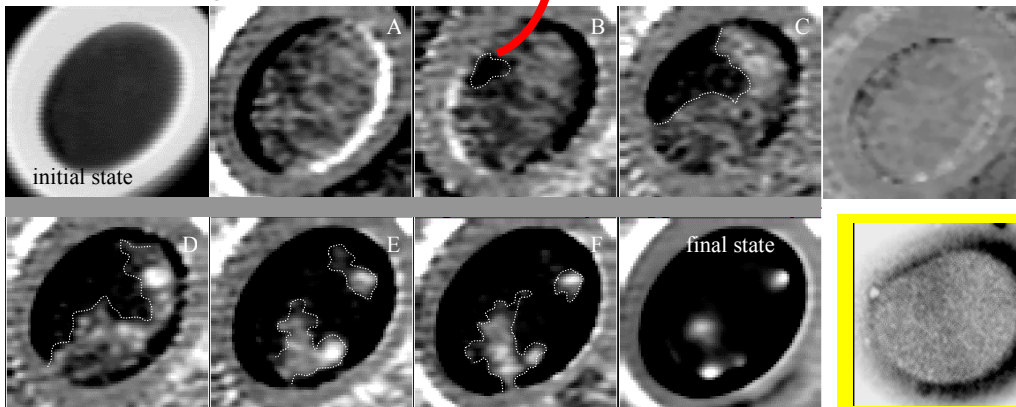
Expulsion of octanol and undecanol *bilayers* in the Surface Forces Apparatus



Imaging the 4 → 2 layering transition



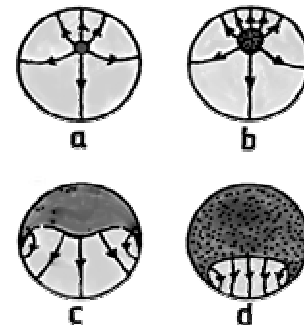
monochromatic light



Movies

$$\text{Squeeze-out time} = m n_a \eta A_0 / 4\pi h_0 P_{\text{ext}}$$

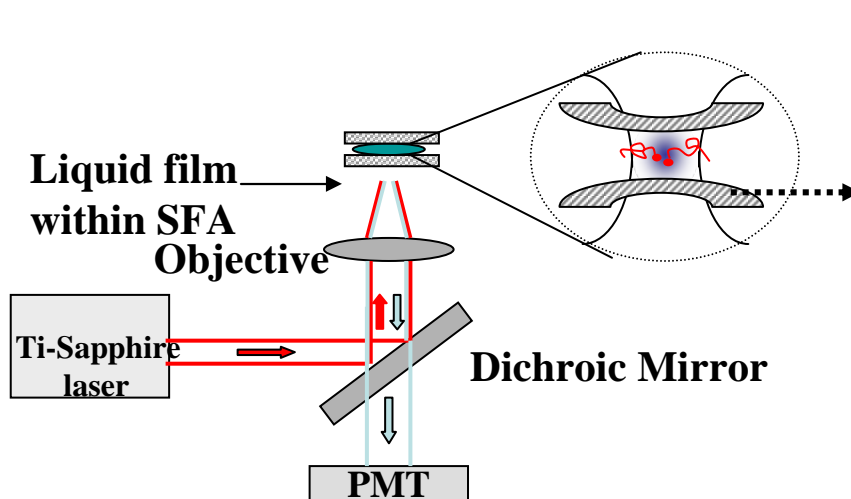
From our data we obtain $\eta = 10^{13} \text{ s}^{-1}$



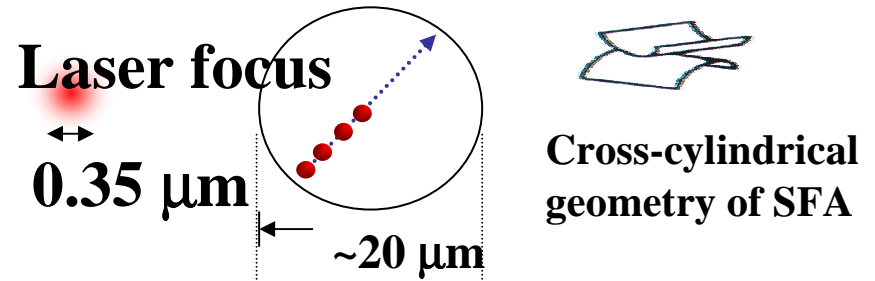
OMCTS: results from F. Mugele, U. Ulm

New Imaging and Spectroscopic Methods: diffusion in confined geometries

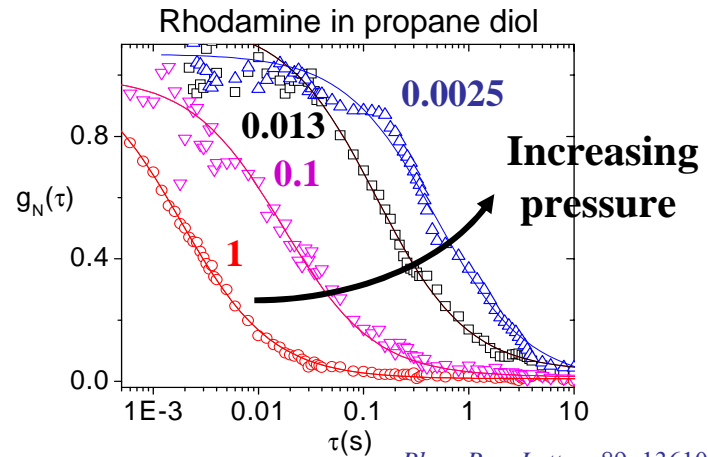
Direct Measurement of Diffusion in Nanometer-Thick Films



**Fluorescence correlation spectroscopy
in a surface forces apparatus**



Autocorrelation function vs. Pressure

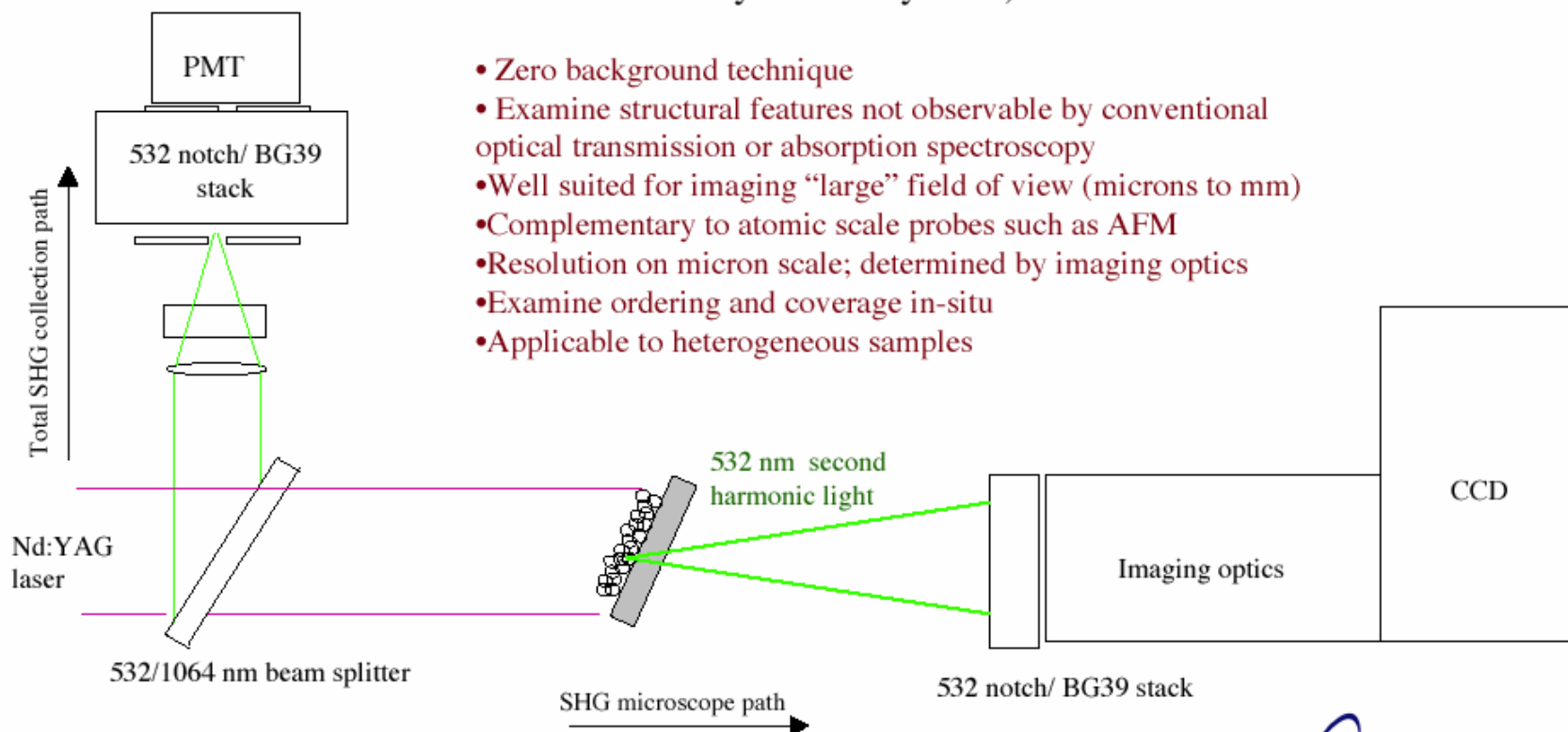


Phys. Rev. Letters **89**, 136103 (2002)

New Imaging and Spectroscopic Methods: SHG imaging

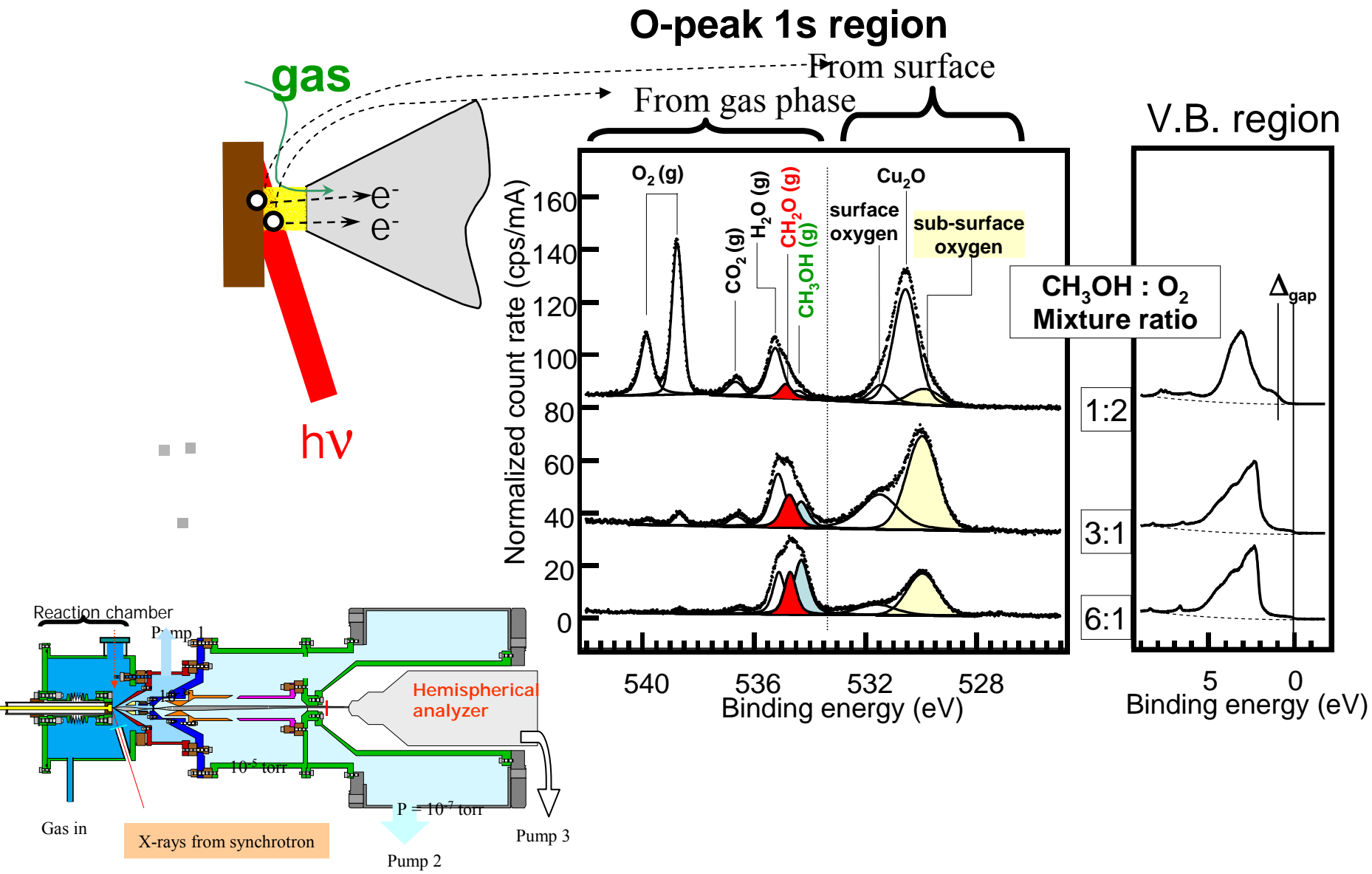
Jeanne M. Robinson and Laura Smilowitz (C-PCS)

SHG microscope developed at Los Alamos National Laboratory for interfacial imaging.
Contrast arises from the symmetry selection rules for SHG (only generated from noncentrosymmetric systems)

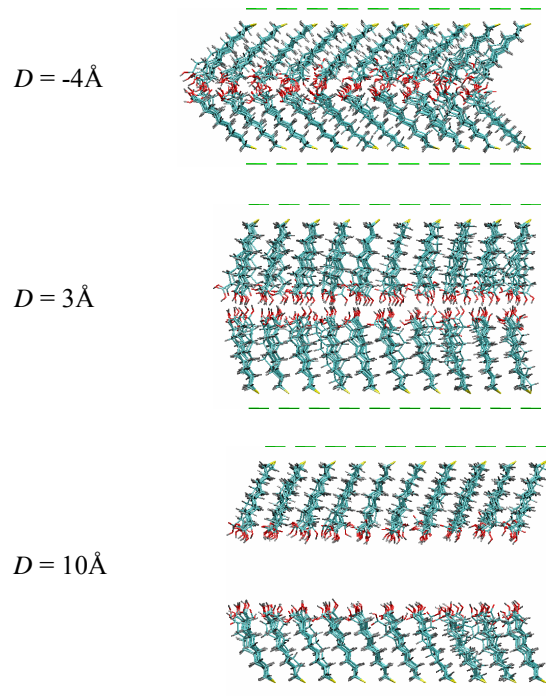


New development:

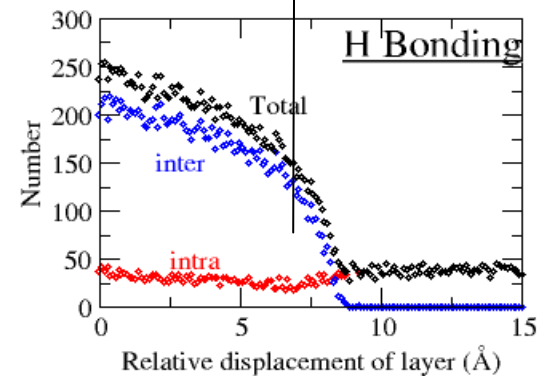
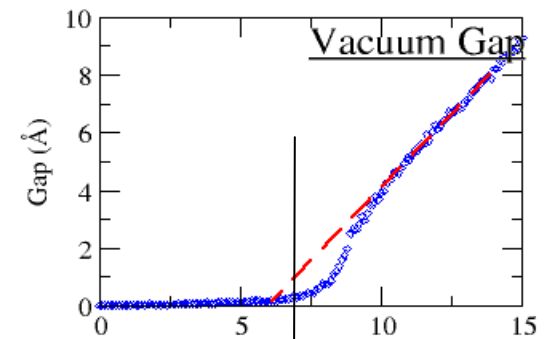
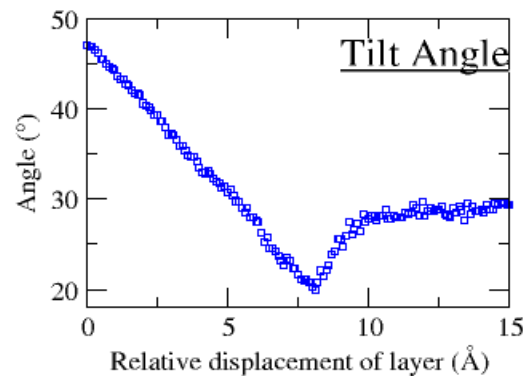
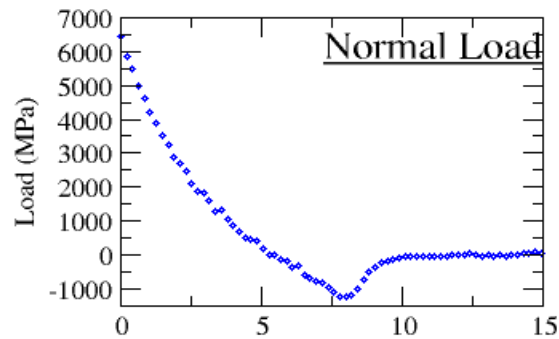
Photoelectron Spectroscopy of surfaces exposed to high pressure of gases (up to 20 Torr)



Theory and computation

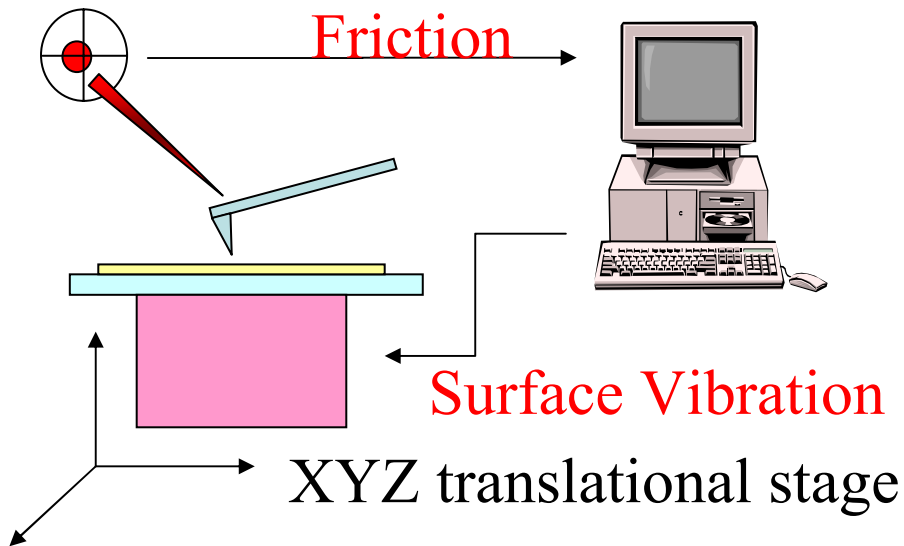


Structure as a function of separation



Control of Friction at the Nanoscale

Yehuda Braiman, ORNL, Marteen de Boer, SNL



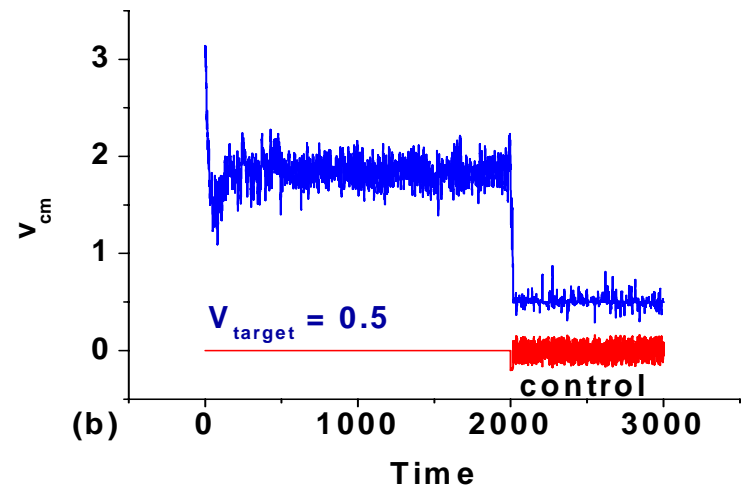
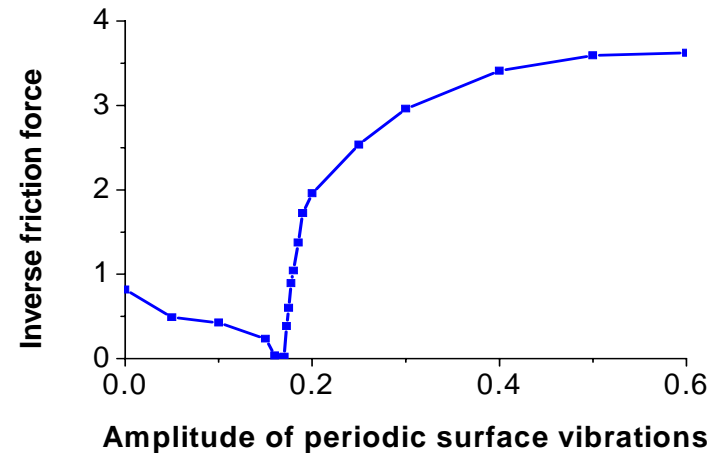
New algorithm developed:

Enables to induce any arbitrarily chosen behavior compatible with the system's dynamics.

*Based on two original concepts:
non-Lipschitzian dynamic
global behavior targeting*

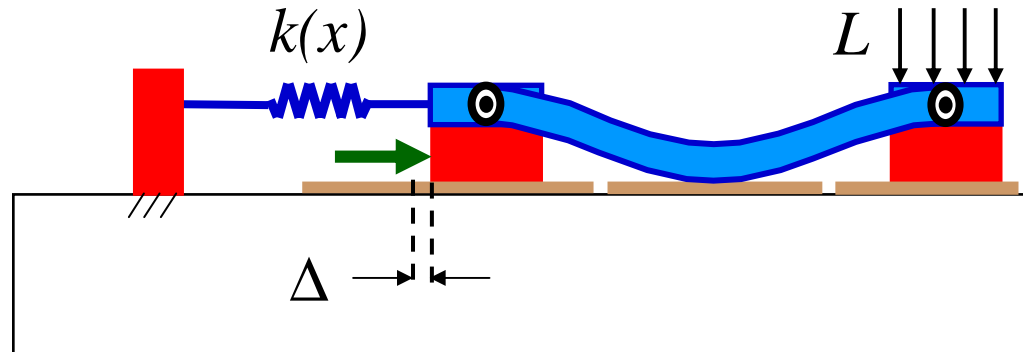
Reference:

Physical Review Letters **90**, 094301 (2003).

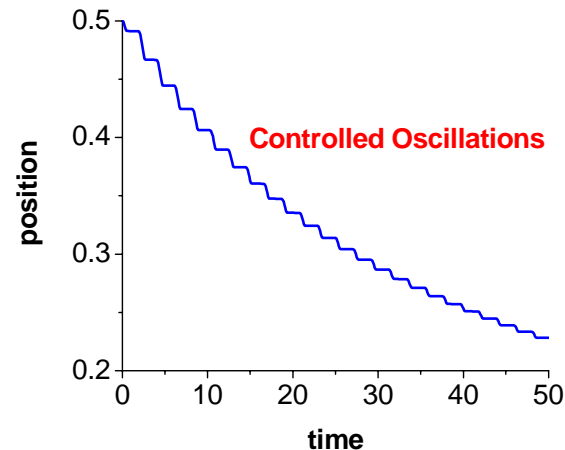
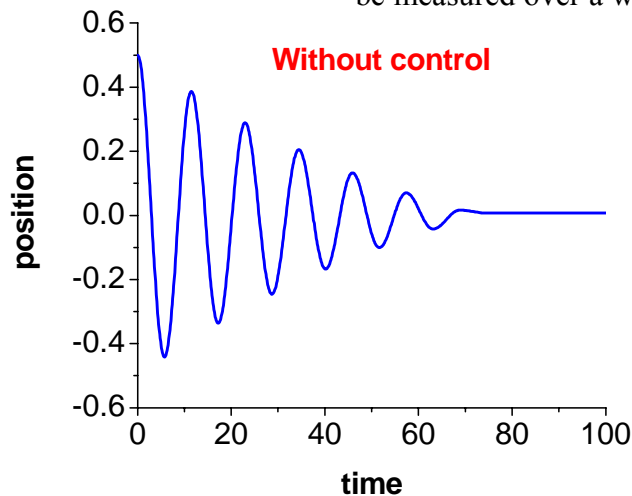


Control of Friction in the Inchworm

Yehuda Braiman, ORNL, Marteen de Boer, SNL



Schematic representation of inchworm, a surface micromachined (MEMS) friction device. The actuation plate is 500 μm long, and the friction clamps are 200 μm long. To walk it, we apply timed signals to the leading clamp, actuation plate and trailing clamp using large values of L , and each step gives a displacement $\Delta \sim 40$ nm. This is a mechanical amplification scheme that achieves high tangential force, allowing friction to be measured over a wide ($\sim 30\times$) range of normal load.



More ongoing group activities ...

Peter Cummings: molecular dynamics simulations of water nano-confined between mica sheets

Michael Kent, Mike Dugger (SNL): neutron reflection experiments (@NIST) to detect water at the interface between SAM lubricants and silicon oxide. Kinetics of hydrolysis of Si-O-Si and rate of degradation of the SAM lubricants in high temperature high, humidity environments

Park, Chandross, Stevens, Grest. (SNL): effect of water on chain conformations and mechanical properties of SAM

... / ...